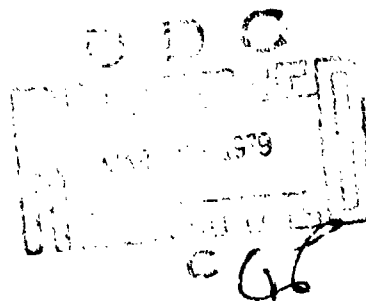


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TECHNICAL REPORT CIVIL ENGINEERING LABORATORY

Naval Construction Battalion Center, Port Hueneme, California 93043

CORROSION AND BIOFOULING OF OTEC
SYSTEM SURFACES -- DESIGN FACTORS

By James F. Jenkins

November 1978

Sponsored by

ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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CORROSION AND BIOFOULING OF OTEC SYSTEM
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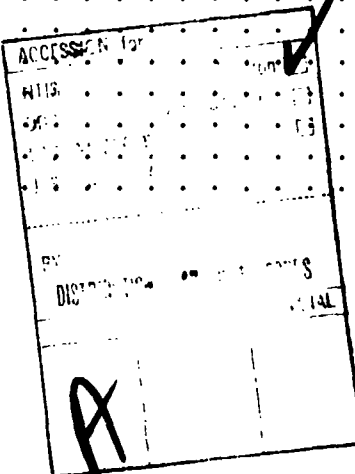
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INTRODUCTION

The biofouling and corrosion of Ocean Thermal Energy Conversion (OTEC) plants are critical factors in the economic feasibility of these plants. Biofouling can decrease heat transfer capacity of the critical heat exchangers, increase pumping requirements due to clogging of pipes and valves, and increase the drag and weight of the platform hull. Corrosion can result in high maintenance and replacement costs and large amounts of downtime. Since OTEC plants are significantly different from any system built to date in both size and operating characteristics, there is little direct experience from which specific anticorrosion or antibiofouling measures can be adopted. Past experience has shown, however, that there are certain basic principles of corrosion and fouling control which, if properly interpreted, can be applied to many specific applications.

Corrosion and biofouling control should be carefully differentiated from corrosion and biofouling prevention. Almost all real industrial plants corrode. Almost all industrial plants that use seawater are subject to biofouling. It has been found that it is not economically feasible to completely prevent corrosion or biofouling. Corrosion and biofouling control is the art/science of maintaining corrosion and biofouling at economically tolerable levels. The basic tactic of corrosion and biofouling control is to identify what levels and types of corrosion and biofouling can be tolerated in specific areas and to control them to those levels. An alternative tactic is to predict the level and type of corrosion and biofouling that will occur and then devise equipment that will tolerate that amount of corrosion and biofouling.

The incorporation of corrosion and biofouling control into the design of any system is essentially an iterative process. A specific design is proposed using available corrosion and biofouling control methods. The results are analyzed to predict corrosion and biofouling behavior. Then the design is modified as necessary until a balance between cost and performance is achieved. The corrosion engineer has at his disposal only two basic tools. He can select a material that has tolerable corrosion resistance in a specific environment or he can modify the environment such that a specific material will have tolerable corrosion resistance. The corrosive environment is not limited to the chemical composition of the corroding substance; it is the "universal environment," which includes all corrosion-related parameters. The biofouling specialist likewise has only two basic tools at his disposal. He can modify the environment so that only tolerable levels of biofouling will occur or he can devise methods for removing biofouling from the surfaces at such a rate that their accumulation is tolerable. Again, the environment in this case is the "universal environment," which includes all fouling-related parameters.

This document will limit its scope to the effect of the "universal environment" on corrosion and biofouling. Since this "universal environment" is a function of system design, the system design should incorporate, where possible, those design features that will result in a "universal environment" which is compatible with the materials and operational requirements of the OTEC plant.

The design factors that influence the "universal environment" are, for the purposes of this report, divided into two broad categories: mechanical and environmental. Mechanical design factors are the combination of size, shape, location, stress, etc., which influence corrosion and biofouling. Environmental design factors are the combination of chemical composition, velocity, flow regime, temperature, pressure, etc., which influence corrosion and biofouling.

The design engineer will find that this document does not give many specific design recommendations. However, it is hoped that the basic design principles described here can be applied to many specific considerations in the design of OTEC systems so that optimum use is made of the existing applicable knowledge of the influence of design on the control of biofouling and corrosion. This report can serve as a basis for the formulation and appraisal of proposed OTEC designs with respect to avoiding improper features and taking advantage of the proper approaches identified.

IMPORTANCE OF CORROSION CONTROL

Good corrosion control can be defined as the achievement of an optimum balance between initial material and equipment costs, maintenance costs, operational requirements, and system life. Achieving good corrosion control will result in optimum long-term overall system efficiency. The critical requirements for good corrosion control, or perhaps more appropriately the adverse effect of poor corrosion control, varies considerably among the various OTEC subsystems.

Heat Exchangers

The heat exchangers for the evaporation and condensation of the working fluid are probably the most critical subsystem of an OTEC plant. The selection of materials for these heat exchangers is limited by the characteristics of the working fluid, the cost of the materials, and their availability in the massive quantities required. Thus, it may be necessary to specifically design the corrosion control for much of the OTEC system around the material selected for the heat exchangers. Corrosion of heat exchangers is a critical problem in all industrial plants, but is a supercritical problem for OTEC. The corrosivity of seawater, the thin-walled tubes required for good heat transfer, the large surface area of material exposed to the seawater, and the adverse effects of mixing seawater with the working fluid all contribute to the supercritical nature of the heat exchanger problem. The availability of heat exchanger maintenance may be limited, unless a large number of

small units are used. However, a large number of small units would cause problems in other areas, such as flow distribution, system complexity, and system efficiency. Thus, heat exchanger maintenance will be, at best, a compromise.

Auxiliary Equipment

The corrosion of auxiliary equipment, such as pumps, piping, valves, turbines, screens, etc., is somewhat less critical than the corrosion of heat exchangers, but is no less important. Corrosion of auxiliary equipment is less critical primarily because there are fewer restrictions on material selection and more options for corrosion control methods. Also, the scale-up factor between existing auxiliary equipment and the size of equipment required for OTEC is not nearly as large as the scale-up factor for heat exchangers. Design for corrosion control of these systems, although perhaps less critical, is more complex as there are such a large number of variables that can be manipulated in the design. The possible effects of system contamination due to corrosion of auxiliary equipment also make the design of these systems more complex.

Support Platform

Corrosion of the support platform is important, but is much more straightforward than for the other systems. This is because of the large amount of experience with similar systems in similar environments. If good standard practices used by marine architects in the design of large ocean-going ships and offshore structures are applied to the design of the OTEC plant, a reliable and efficient support platform can be built. This must not be interpreted to indicate the design of corrosion control for the OTEC support platform will not present complex and unique problems; only that these problems can most likely be solved by the application of well-known corrosion control techniques.

IMPORTANCE OF BIOFOULING CONTROL

As for corrosion control the successful control of biofouling can be defined as the achievement of an optimum balance between initial material and equipment costs, maintenance costs, operational requirements, and system life. Achieving good biofouling control will result in optimum long-term overall system efficiency. It should be re-emphasized that biofouling control is not biofouling prevention or elimination. Biofouling control is simply the capability of limiting biofouling accumulations to levels that can be operationally tolerated. The amount of biofouling accumulations that can be tolerated in the various OTEC subsystems varies considerably. Thus, the requirements and techniques for biofouling control will vary considerably among these subsystems.

Heat Exchangers

As the heat exchangers for evaporation and condensation of the working fluid in an OTEC plant must transfer a large amount of heat at very low temperature gradients, the presence of even thin films on the heat exchanger surfaces will seriously degrade heat exchanger performance. The presence of macrofouling organisms in the heat exchangers is important because of clogging, crevice, and turbulence effects. Macrofouling is, however, not the critical problem. Even the thin, soft films of microfouling are sufficient to cause enough degradation in heat exchanger efficiency to seriously affect the OTEC power cycle. (See p 32 for detailed explanation.) Because the control of microfouling usually results in the control of macrofouling, microfouling control will be the key factor in biofouling control of OTEC heat exchangers.

The evaporators in an OTEC plant will utilize warm, oxygen-rich and biologically active surface waters, while the condensers will use cold, oxygen-poor, nutrient-rich, biologically less active waters from depths of 600 meters (2,000 ft) or more. Because the evaporator and condenser will operate with seawater of different chemical, physical, and biofouling characteristics, it is probable that the most effective biofouling control techniques will be different for these subsystems. It has been assumed, but not necessarily proven, that biofouling of the condensers will be less of a problem than biofouling of the evaporators. Although this may not be the case, it is certain that the biofouling control for each of the systems should be approached with these potential differences in mind.

Auxiliary Equipment

The biofouling of auxiliary equipment, such as pumps, piping, valves, screens, etc., has a less immediate impact on the operation of an OTEC plant than biofouling of the heat exchangers, but it must be considered in order to obtain efficient long-term operation. Macrofouling will probably be the major factor in biofouling of auxiliary OTEC equipment, because this type of equipment usually has a high tolerance for microfouling. Macrofouling, however, can cause restriction of fluid flow, turbulence, and other problems in piping systems. It can also cause restriction, clogging, or jamming of valves, screens, and pumps; particularly when they are operated intermittently. The mass of macrofouling accumulations can even cause problems in rotating machinery due to an increase in rotating mass or an imbalance condition.

The control of biofouling in the auxiliary equipment of an OTEC plant may be in some ways more difficult than biofouling control for the heat exchangers. Due to the wide variety of auxiliary equipment and biofouling control requirements and techniques applicable to each component, the implementation of an overall biofouling control program for the auxiliary equipment will be complex.

Support Platform

Biofouling of the support platform will have little immediate effect on the operation of an OTEC plant; however, long-term effects may be significant. The increased drag of the platform due to biofouling will result in increased power requirements for relocation or dynamic station keeping. If the plant is moored, the forces on the mooring system could significantly increase due to increased drag. The mass of fouling accumulations can also change draft and trim of the support platform. Biofouling of the support platform can also cause clogging of seawater intakes and other through-hull connections.

While the biofouling of an OTEC support platform will be similar to that encountered on large ships and fixed ocean platforms, there are significant differences between the operation of OTEC and existing ships and platforms that may lead to significant differences in biofouling and biofouling control requirements. Ships normally operate at significant velocities in the open ocean and are normally at rest in harbors that are, to some extent, polluted and are not typical of the open ocean. Because of high fuel costs, the drag induced by biofouling is a significant factor in the economy of ship operation; therefore, biofouling is controlled at low levels. The significance of biofouling on the operation of fixed ocean platforms is much less than that for ships, so it is normally not controlled. OTEC platforms will operate at very low velocities in the open ocean but, as discussed above, the effect of biofouling on the OTEC platform may be significant. Thus, biofouling control for the OTEC support platform must be based upon existing experience with biofouling of similar structures. However, this experience is not directly applicable and must be adapted to unique OTEC plant operations and requirements.

DESIGN FACTORS INFLUENCING CORROSION

The "universal environment" experienced by a metal will determine its corrosion behavior. By avoiding those design features that lead to an aggressive "universal environment," the corrosion of an OTEC plant can be significantly reduced. Proper design, combined with other corrosion control measures, will result in an OTEC plant with optimum resistance to deterioration.

The design factors that influence the "universal environment" can be divided into two broad categories: mechanical and environmental. Factors discussed under these broad categories often have significant effects on the various forms of corrosive attack discussed in the Appendix. If the acceptable forms and rates of attack and the design factors influencing them are considered, most adverse conditions can be avoided.

Mechanical Design Factors

Mechanical design factors are those conditions of the metal substrate that influence the "universal environment" and, thus, the corrosion behavior of the metal. This influence may be direct, as in the case of the effect of induced stress on stress corrosion cracking, or it may be indirect, as in the case of the effect of equipment layout on maintainability and, thus, tolerance of corrosion.

Geometry and Orientation. The broadest category of mechanical design factors that influence corrosion is geometry. By proper control of geometry a given material can be allowed to exhibit its best corrosion resistance. All alloys can be made to corrode if the proper, or rather, improper, conditions of exposure are present. If the conditions under which a given alloy is susceptible to corrosion are known, these conditions can be avoided or controlled.

Certain basic principles of corrosion can be applied to the selection of proper geometry for a given function and material. The first of these principles is that any difference in condition between different areas on a given member can lead to accelerated attack by a differential environment cell. These differences can be direct, such as bimetallic or multimetallic connections, or they can be subtle, such as in attack due to crevices.

Whenever two or more dissimilar metals are placed in electrical contact and exposed to a conductive environment, intolerable galvanic attack may occur. Therefore, its effect must be carefully considered. Several basic factors control the direction and magnitude of galvanic attack which will occur in such a couple. The first is the position of the material on the electrochemical potential scale for the exposure conditions. Such a list is given in Table 1. This so-called "Galvanic Series" has been developed from many experiments and experiences with bimetallic couples in seawater. Materials listed near the top of the series are active, or anodic, with respect to the more noble, or cathodic, materials below them on the list. In general, the greater the separation between the alloys on the list, the more severe the galvanic attack on the anodic material will be. This galvanic series is for surface seawater and is directly applicable only in that environment. Considerable deviation from this series is possible in environments significantly different than surface seawater. Galvanic series for these other environments are generally not well developed; they remain to be developed from related experience or experiment.

The actual rate of galvanic attack is dependent on many undetermined factors, and, thus, a specific rate of attack cannot be predicted. However, several geometric factors can be manipulated to minimize the adverse effects of galvanic coupling. The first of these is area ratio. The most severe galvanic attack will occur when the exposed area of the cathodic material is large with respect to the exposed area of anodic material. Even when the materials involved in the couple are fairly close in the galvanic series, the rate of galvanic corrosion can be high if the area ratio is adverse. Thus, it is good design practice to avoid

galvanic couples where possible and, when they cannot be avoided, to make the exposed anodic area large with respect to the exposed cathodic area. A typical case where adverse anode/cathode area ratios are inadvertently designed into a system is when an innocuous galvanic couple is improperly coated. Uninformed logic would indicate that the more corrodable material could be left bare while the more corrodable material should be coated. When coating defects occur on the coated area, then a small anode/large cathode situation occurs. Thus, when coating a galvanic couple, coat both materials or coat the cathode only. To coat the anode only is to invite rapid attack.

Galvanic effects can be used to advantage in many applications. When a critical system component is relatively small it can be fabricated from a material that is cathodic to the material from which the bulk of the system is fabricated. Thus, the critical component will receive cathodic protection from the bulk of the system. The acceleration of corrosion of the relatively large exposed area of the bulk system will be minimal. This technique is commonly applied. Examples are cathodic "trim" seats, discs and stems of valves having anodic bodies, and cathodic impellers, shafts and wear rings of pumps with anodic casings.

An additional factor influencing the rate of galvanic attack is external circuit electrical resistance. As shown in Figure 1, a galvanic cell is essentially a battery/load system. When the intermetallic resistance, R_1 , or the environmental resistance, R_2 , is raised, the current flow, I_0 , is lowered, thus reducing the amount of galvanic corrosion. Thus, the distance between the active members of a couple should be maximized when possible. Also, insulating or high resistance bushings, etc., can reduce or eliminate galvanic corrosion.

Concentration cell corrosion is similar to galvanic corrosion in that it is a result of an electrochemical difference between electrically connected portions of a member. However, in concentration cells this electrochemical difference is due to a difference in environment rather than a difference in substrate composition. In seawater, the most common form of concentration cell attack is crevice corrosion. In this form of attack, seawater is trapped within small gaps and stagnates. Either the consumption of a constituent of the solution, such as oxygen, or the buildup of a substance, such as a metal ion, leads to a significant difference in environment between the inside of the crevice and the outside. According to LaQue (Ref 1, p 39), metals near the top of the galvanic series, such as iron, tend to crevice corrode by the oxygen starvation type of attack, while materials, such as copper (low on the galvanic series), tend to crevice corrode by the metal ion concentration type of attack. Alloys near the middle of the galvanic series, such as the copper-nickel alloys, are less susceptible to crevice attack. Alloys, such as stainless steels, which exhibit a more noble potential than their constituents, are often particularly sensitive to oxygen starvation attack.

Table 1. Galvanic Series in Surface Seawater

| | |
|--|---------------------------------------|
| | Magnesium |
| | High Purity Aluminum |
| | Zinc |
| | Galvanized Steel (New) |
| | Aluminum Alloy 5052 |
| | Alclad Aluminum (X7002) |
| | Aluminum Alloy 3003 |
| | Aluminum Alloy 6061-T6 |
| | Aluminum Alloy 7079-T6 |
| | Aluminum Alloy 2024 |
| | Cadmium |
| | Cadmium Coated Steel (New) |
| | Mild Steel |
| | Wrought Iron |
| | Alloy Steel |
| | Cast Iron |
| | Ni-Resist Cast Iron |
| | Monel Alloy 400 (active) |
| | Stainless Steel 410 (active) |
| | Stainless Steel 430 (active) |
| | Solder (60% Pb - 40% Sn) |
| | Stainless Steel 304 (active) |
| | Stainless Steel 316 (active) |
| | Stainless Steel Alloy 20-Cb (active) |
| | Lead |
| | Tin |
| | Muntz Metal |
| | Manganese Bronze |
| | Naval Brass |
| | Nickel (active) |
| | Inconel 600 (active) |
| | Yellow Brass |
| | Aluminum Bronze |
| | Red Brass |
| | Copper |
| | Silicon Bronze |
| | Nickel Silver |
| | Cupro-Nickel 95-5 |
| | Cupro-Nickel 90-10 |
| | Cupro-Nickel 80-20 |
| | Cupro-Nickel 70-30 low Fe |
| | Cupro-Nickel 70-30 high Fe |
| | G-Bronze |
| | M-Bronze |
| | Nickel (passive) |
| | Inconel 600 (passive) |
| | Silver Solder |
| | Monel (passive) |
| | Stainless Steel 410 (passive) |
| | Stainless Steel 430 (passive) |
| | Stainless Steel 304 (passive) |
| | Stainless Steel 316 (passive) |
| | Stainless Steel Alloy 20-Cb (passive) |
| | Stainless Steel A16X |
| | Silver |
| | Inconel 625 |
| | Hastelloy C |
| | Titanium |
| | Graphite |
| | Gold |
| | Platinum |

NOTE: In general, the greater the separation between alloys, the more severe the galvanic attack will be on the anodic material.

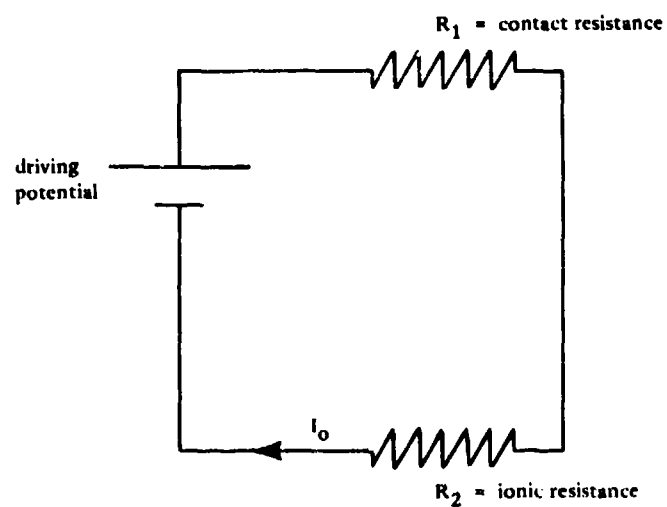
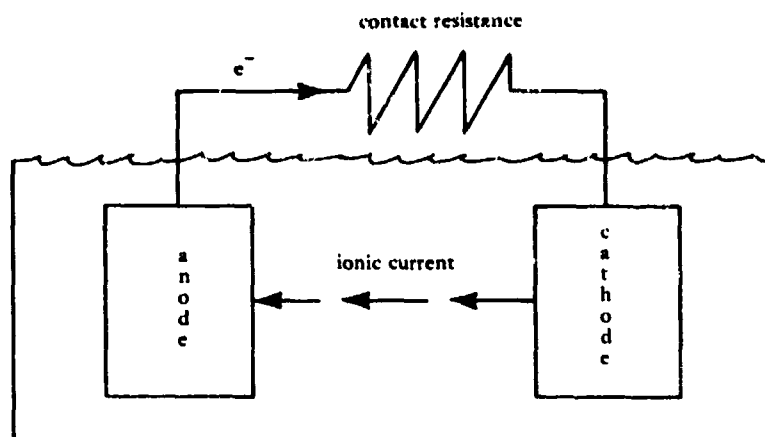


Figure 1. Galvanic corrosion equivalent circuit.

The most reliable technique for avoiding crevice corrosion is to avoid crevices. Crevices from bolted or riveted joints (Ref 2, p 17), gasketed joints (Ref 1, p 164), discontinuous welds or welds without full penetration (Ref 2, p 17) as well as other situations where solutions can be trapped or held should be avoided where materials susceptible to crevice corrosion are used. Good design practice for OTEC systems is to use continuous, full penetration welds wherever possible. When bolted or other lap type joints are required, a nonwater absorbing gasket material (Ref 2, p 20) should be placed between the mating surfaces. When such gaskets are used, they should be carefully sized and placed in order to avoid aggravating crevice attack (Ref 3, p 10.16). The effect of a poor gasket fit is shown in Figure 2. Nonwater absorbing caulking materials, such as silicone rubber, can also be used to seal crevices when the crevices cannot be avoided. Such gasket design features cannot prevent crevice attack on vulnerable materials, such as most stainless steels and some copper alloys. Special attention should be given to all joints of this type to avoid crevice attack by using nonvulnerable materials or proper sealants, or by substituting an alternative connection method.

Another concentration cell related type of attack is caused by surface contamination. The accumulation of sediments, corrosion products, or other contaminants on metal surfaces often leads to concentration cell type attack (Ref 3, p 10.16). A system that is clean, will remain clean, or can be easily cleaned will be more corrosion free than a system that will accumulate and hold contaminants (Ref 2, p 15). There are a multitude of structure geometries that can lead to the trapping and holding of contaminants. Figures 3 (Ref 3, p 10.15) and 4 (Ref 2, p 25) show typical situations where contaminant trapping is likely and recommended alternative practice.

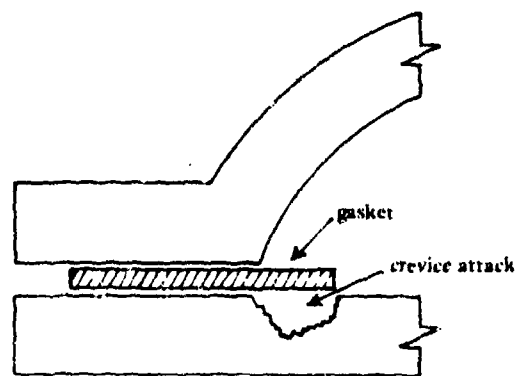
Interfaces between gases and liquids, such as is present in partially filled tanks, are frequently the site of corrosion (Ref 2, p 27). Piping and tanks should be designed so that they are completely full of either liquid or gas. Figure 5 shows typical situations of this type and recommended alternative practice.

Erosive damage can also occur from vapor impingement, especially if droplets of condensed liquid are present. Proper baffling of the vapor stream can be used to prevent this type of attack.

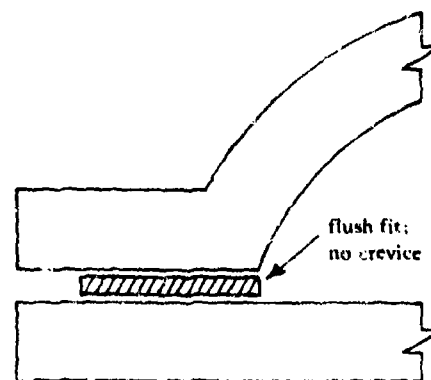
In general, smooth flow conditions in piping systems are desirable to reduce corrosion due to impingement and other forms of turbulence-related attack. Desirable piping designs, such as those shown in Figure 6 (Ref 2, p 29), should be used whenever practical.

Dead ends, where stagnation can occur, should be avoided whenever possible. When they cannot be avoided, the dead end should enter from the top of a line or tank in order to minimize contaminant buildup (Ref 2, p 27). The placement of valves in horizontal runs of piping rather than in vertical runs also minimizes corrosion from this effect (Ref 2, p 27).

Structural geometry also affects the performance of protective coatings. Sharp corners are to be particularly avoided on structures that are to be painted. In Figure 7 the effect of sharp corners on coating thickness is shown (Ref 3, p 10.22).

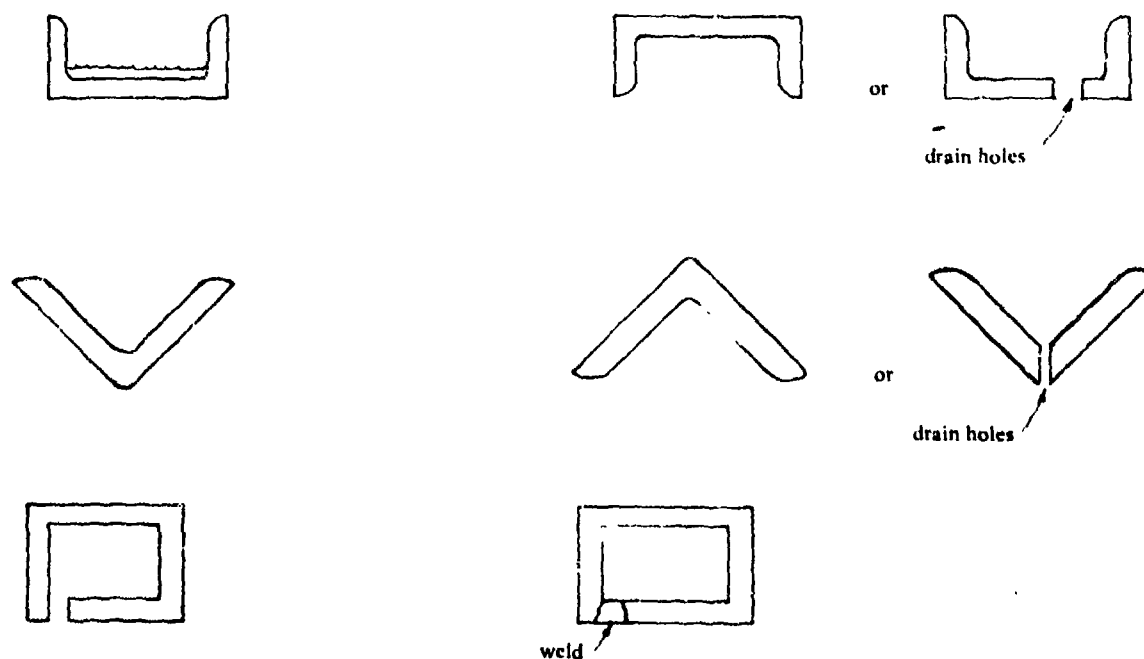


Poor Practice



Good Practice

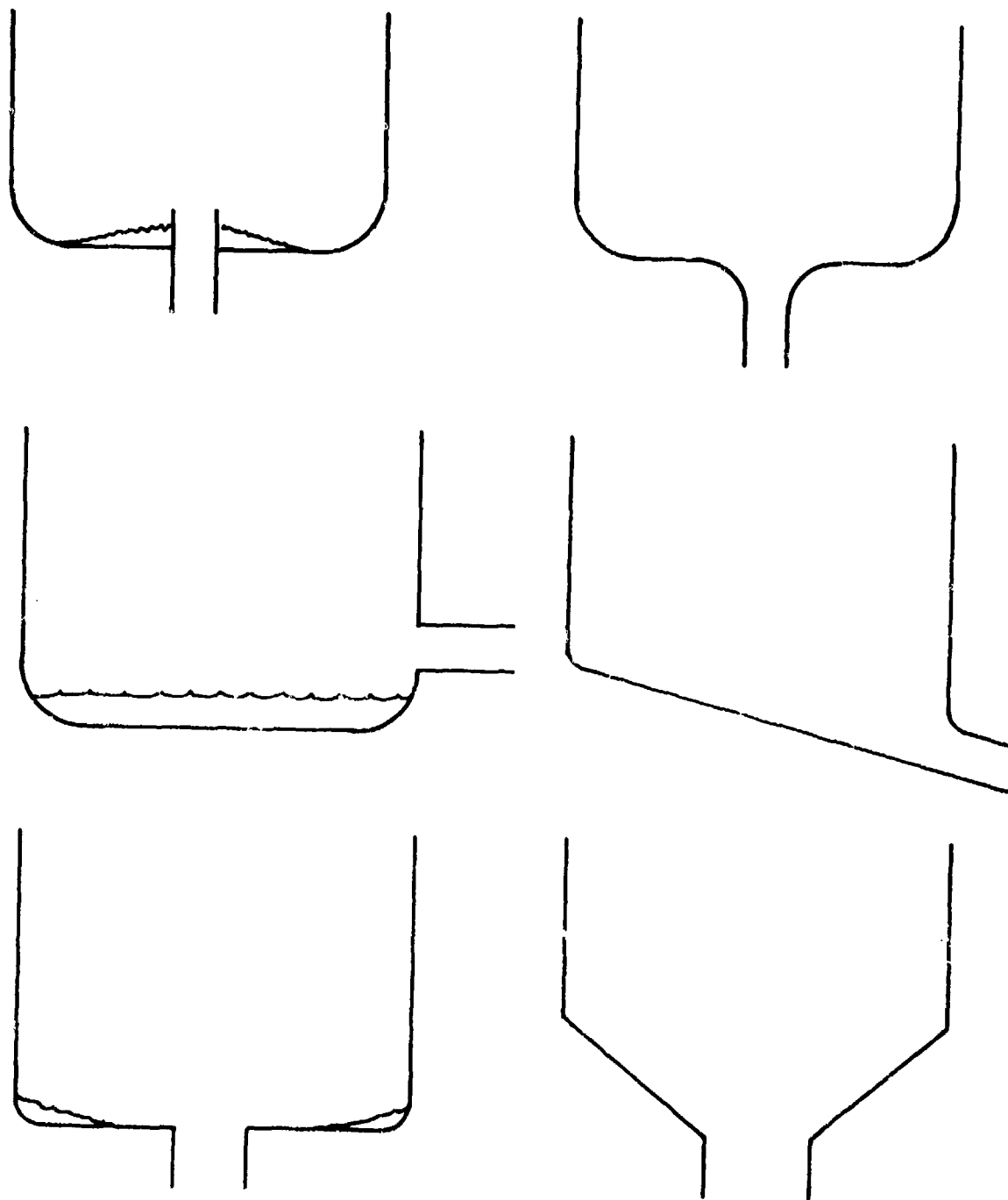
Figure 2. Effect of gasket fit.



Poor Practice

Good Practice

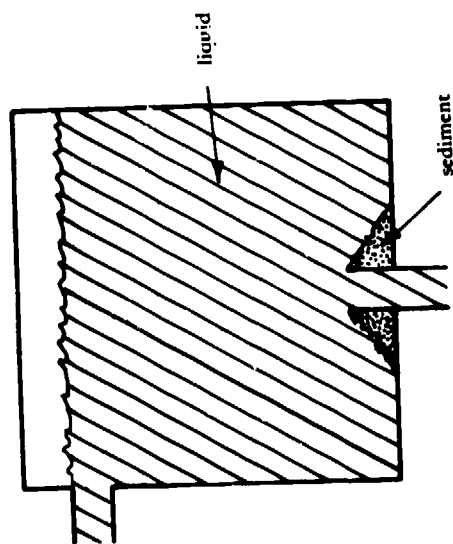
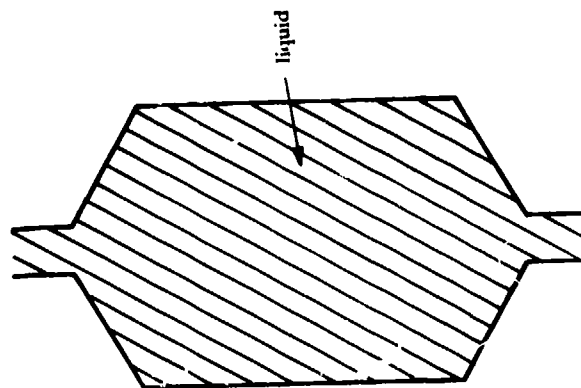
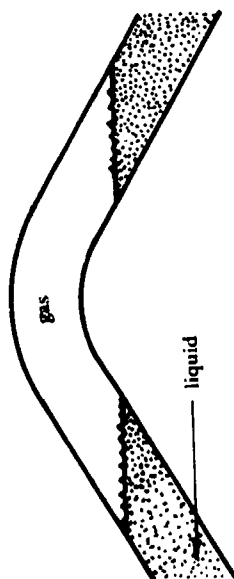
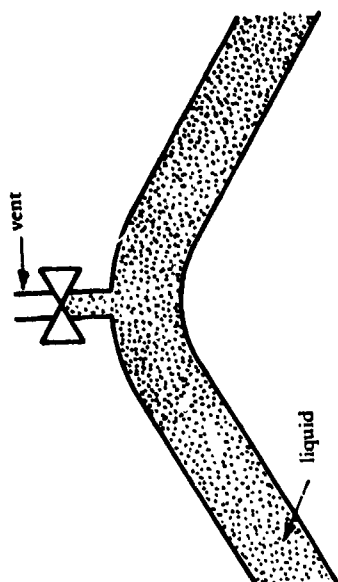
Figure 3. Structural member effects.



Poor Practice

Good Practice

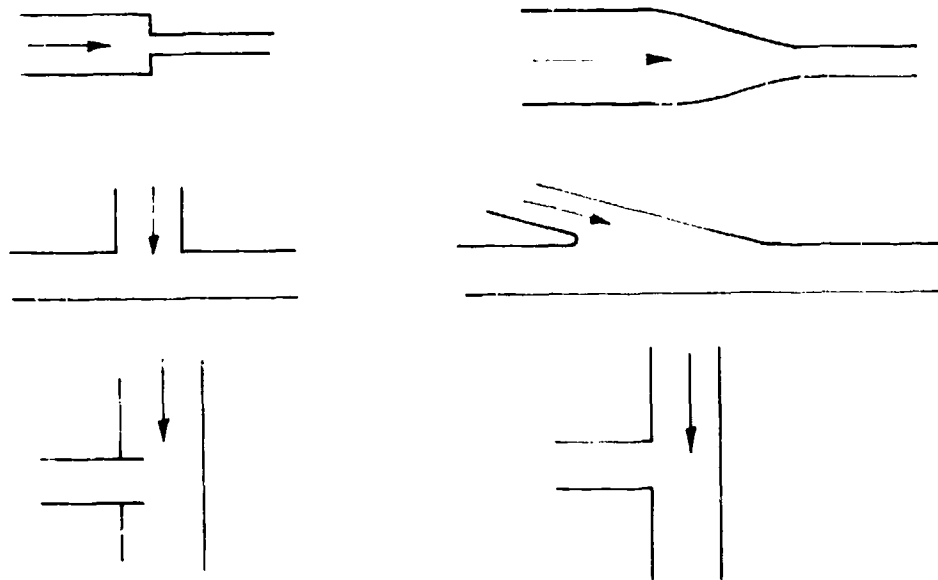
Figure 4. Tank drain effects.



Good Practice

Poor Practice

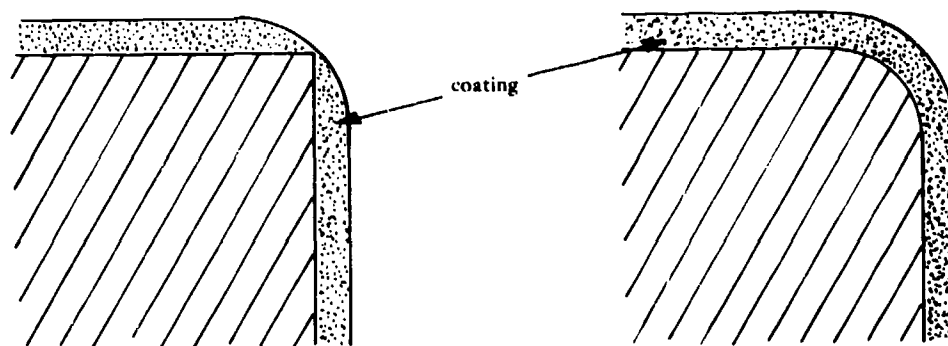
Figure 5. Liquid-gas interface effects.



Poor Practice

Good Practice

Figure 6. Piping design effects.



Poor Practice

Good Practice

Figure 7. Effect of sharp edges on coating thickness.

Surface orientation with respect to the horizontal also has an effect on corrosion. This is primarily due to the accumulation of corrosion products or sediments on the upper side of horizontal surfaces. Proper system geometry that minimizes contamination due to accumulation of corrosion products and sediments and maximizes the maintainability and cleanability of these surfaces will minimize the adverse effects of surface orientation.

Other geometry-related design factors should be considered in the design of OTEC systems. Such an example is the possibility of corrosion fatigue induced by structural vibration (Ref 4, p 163). In general, a simple design is preferable to a complex one. This includes the reduction of the number of structural members whenever possible, particularly in areas where corrosion is a problem. Redundant members in a corrosive zone usually only result in redundant failures rather than in added safety. A simple design, easy to maintain and repair, which avoids dissimilar metal connections, crevices, etc., will maximize the service life of properly selected materials.

Layout. The layout of equipment in an OTEC plant will have little direct effect on the corrosion of the equipment. However, the indirect effects on service life can be significant. The most important factor in the relationship between layout and service life is cleanability and maintainability. A system that is easy to clean and maintain will normally receive more frequent and thorough care than a system that is difficult to maintain. Convenient access to maintenance points is primarily a function of layout and is an important design factor. Convenient access to and ease of replacement of failure-prone components will also reduce system downtime and unexpected failures. For equipment that must be drained for cleaning and maintenance, proper geometry such as that indicated in the previous section will allow for complete drainage and easy flushing of cleaning residues.

Not only is easy access to equipment important for cleaning and maintenance, but it is also important in order to be able to properly inspect and assess the equipment or structure for cleaning, maintenance repair, or replacement. Proper cleaning and maintenance schedules can often only be derived from the results of thorough, carefully planned inspections. Proper inspections also have the beneficial effect of reducing downtime due to unexpected failures.

One possible direct effect of equipment layout on corrosion is that of metal ion contamination. Metal ion contamination of the environment can significantly accelerate the corrosion of some materials, especially aluminum alloys. Even very small amounts of copper from the corrosion of copper-containing alloys will deposit on the surfaces of aluminum alloys and result in rapid attack of the aluminum (Ref 1, p 19). This effect can be prevented by eliminating the source of metal ions or by locating the equipment such that the copper ions are produced downstream of the aluminum alloy components. Thus, if flow is maintained, the copper salts will not contact the aluminum alloys. Another potential source of copper salts are the copper-containing antifouling coatings;

these coatings should be avoided on aluminum structures (Ref 1, p 19). Other metal ion contamination problems exist with mercury and aluminum, and mercury and copper.

In some cases, the effect of dissolved metal salts can be beneficial. Iron salts can reduce the corrosion of certain copper alloys (Ref 5). Also, corrosion products from aluminum and zinc have been reported to have certain beneficial effects on the corrosion of steel (Ref 6).

Surface Finish. No studies of the effect of surface finish on the behavior of metals in seawater were located in the literature survey performed for this report. However, surface finish can be expected to have some effect on the corrosion behavior of some materials. Materials susceptible to crevice corrosion will probably suffer more extensive attack when exposed in a mechanically roughened condition. This is due to the large number of crevices formed during the roughening process. This is similar to the adverse effects of sheared edges on the corrosion behavior of similar materials (Ref 7, p 89).

Another effect not directly related to surface finish, but with a similar result to the effect of sheared edges is the orientation of the exposed grain on corrosion behavior. Most materials are anisotropic in both their mechanical and chemical behavior. Some aluminum alloys are particularly anisotropic in their corrosion behavior (Ref 8). In these alloys, corrosion attack is many times greater in the longitudinal direction (parallel to grain orientation) than in the transverse direction (perpendicular to grain orientation). An extreme example of this form of attack is the exfoliation attack noted on some very high strength aluminum alloys (Ref 7, p 190); the corrosion products exert sufficient pressure to delaminate the material, resulting in catastrophic attack.

Stress. Tensile stresses below the level required for plastic deformation of the metal, or surface films (such as mill scale or protective corrosion products) do not change the rate of general corrosion of metals exposed to seawater (Ref 9, p 236). The presence of a corrosive agent, such as seawater, can, however, significantly reduce the load-carrying capability of metals, even when no significant general attack occurs. Also, a given amount of corrosion damage on a highly stressed member will usually have more serious consequences than the same amount of damage on a member with lower applied stress.

The reduction of the ability of a member to sustain a static stress when exposed to a corrosive environment is defined as stress corrosion cracking. While the mechanism of this phenomenon is, at best, poorly understood, the effects of a given corrosive environment on the static load-carrying capacity of a given material can be well defined by the use of fracture mechanics. As all engineering structures contain flaws, test results of stress corrosion cracking coupled with fracture mechanics can be used to determine the maximum flaw size that can be tolerated in a given material and to define the level of inspection required to locate flaws of this critical size.

The following materials are recognized to be susceptible to stress corrosion cracking in marine environments (Ref 10, p 3).

1. High strength steels
2. Austenitic stainless steels
3. Precipitation-hardened stainless steels
4. Quenched and tempered Martensitic stainless steels
5. High strength titanium alloys
6. High strength aluminum alloys
7. Copper zinc alloys (brasses)
8. Aluminum bronzes
9. Manganese bronzes

The susceptibility of high strength steels to stress corrosion cracking is related to the strength of the material. For a given alloy composition, the higher the strength level, the greater the susceptibility to stress corrosion cracking. Stress corrosion cracking is the principal limiting factor in the strength level of steels that can be used safely in seawater (Ref 1, p 216). Austenitic stainless steels are susceptible to stress corrosion cracking in seawater when they have become sensitized to intergranular corrosion by improper heat treatment or improper welding techniques (Ref 1, p 221). The avoidance of sensitization by heat treatment or alloy additions is well documented (Ref 11) and can essentially eliminate this form of attack. Austenitic stainless steels can suffer stress corrosion cracking in seawater even when not sensitized if the temperature of the seawater is above about 140°F and there is an opportunity for concentrations of chlorides in crevices, in splash areas, or under insulation. These critical conditions should not be encountered in OTEC components operating well below 140°F. The resistance of austenitic stainless steels to stress corrosion cracking is influenced also by alloy composition. A high nickel content is especially desirable. The 25% nickel content of Al6X alloy is high enough to prevent stress corrosion cracking under OTEC conditions.

The precipitation hardening stainless steels are also susceptible to stress corrosion cracking. The susceptibility of these alloys is, as for the alloy steels, a function of the strength level. Alloys heat-treated to high strength levels, particularly when age-hardened at temperatures below about 1,000°F, are most susceptible (Ref 7, p 134).

The quenched and tempered martensitic stainless steels when hardened above about 32 Rockwell C are susceptible to stress corrosion cracking in seawater (Ref 12, p 33).

The stress corrosion behavior of titanium alloys in seawater is well documented (Ref 7,10,13-17). The incidence of stress corrosion cracking of titanium alloys in marine service has been low because of the use of resistant alloys, the low stress levels encountered, the knowledge from earlier failures, and the application of the results of

laboratory studies. Future failures can be avoided by the use of alloys known to be resistant to this form of attack under the conditions of exposure (Ref 15, pp 1-2).

Aluminum alloys, particularly the high strength alloys, are also susceptible to stress corrosion cracking in seawater (Ref 1,7,18,19). As is the case for titanium alloys, only those aluminum alloys that have been found to be resistant to stress corrosion cracking in seawater should be used in applications where stress corrosion cracking would result in component failure.

Copper zinc alloys are susceptible to stress corrosion cracking in seawater (Ref 1, p 223). The presence of ammonia, even in very small concentrations, greatly increases the severity of this attack (Ref 20, p 147).

The 90:10 copper-nickel candidate alloy CA706 is not susceptible to stress corrosion cracking in seawater or in ammonia-contaminated seawater.

Aluminum bronzes are also susceptible to stress corrosion cracking in seawater. Heat treatment or nickel additions can effectively eliminate this effect (Ref 1, p 223). Ammonia also can be expected to accelerate this attack.

Careful consideration must be given to the use of alloys in an OTEC plant that are susceptible to stress corrosion cracking. Unless further testing shows the material to be suitable, it should not be used in an OTEC plant. Usually the stresses induced during fabrication of a structure are as serious in leading to stress corrosion cracking as are applied loads (Ref 19, p 18).

The reduction of the ability of a member to sustain a dynamic stress when exposed to a corrosive environment is defined as corrosion fatigue (Ref 21, p 148). The combined effect of corrosion and fatigue produces an adverse conjoint action that leads to premature failure (Ref 22, p 1). Any material that is subject to corrosion in seawater will be affected by corrosion fatigue to a greater or lesser extent. Corrosion fatigue test data, preferably coupled with actual service experience in seawater, must be considered to predict the service life of materials under the conditions of cyclic loading expected in an OTEC application.

Cathodic Protection. Cathodic protection can reduce, or in some cases eliminate, corrosion of materials in seawater. While the design of cathodic protection systems is outside the scope of this report, several factors in overall system design can affect the applicability of cathodic protection. A system that is designed according to the principles outlined earlier will not only result in a system that is inherently more corrosion-resistant, but it will also result in a system that is easier to cathodically protect.

In general, cathodic protection can be applied easily to external surfaces of components continuously immersed in an electrolyte, such as seawater. The more complex the surface geometry, the more difficult the design of the cathodic protection system will be. The internal portions

of large tanks, condenser waterboxes, pipes, etc., can be cathodically protected. The internal surfaces of small diameter tubes can be cathodically protected if there is no fluid flow in the tubes (Ref 23).

Specific criteria for cathodic protection of large steel structures are well defined (Ref 24-28). Specific criteria for cathodic protection of some stainless steels, copper alloys, aluminum alloys, and nickel alloys have been developed (Ref 28-32), but they have not been validated to the extent of the criteria for protection of steel structures.

Protective Coatings. Protective coatings are widely used in the marine industry to mitigate corrosion of structures and equipment. For equipment exposed to the marine atmosphere, protective coatings can provide long-lasting protection, if they are properly selected and properly applied to well-designed structures. Good design practices, as outlined previously, allow for easy access for metal preparation and coating application, and for periodic inspection and maintenance. Simple designs with rounded corners allow for uniform application of the selected coatings. It must be remembered that all protective coatings will contain defects, and that the coatings will deteriorate with time. Thus, unless additional protection is provided, corrosion will occur at coating defects. This is of particular concern on alloys that corrode nonuniformly.

Protective coatings on submerged surfaces often serve a dual or treble purpose. The primary objective of applying the coating is to isolate the environment from the metal and, thus, eliminate corrosive attack. However, with simple and always imperfect barrier coatings, corrosion will continue at the coating defects at least at its normal rate. When a barrier coating is combined with a cathodic protection system, a dual benefit is achieved. The cathodic protection system needs only to protect the areas where coating defects or deterioration have exposed the underlying material. While there is considerable controversy over the economic merits of the combination of these two protective systems, it is generally recommended that cathodic protection of large, submerged surfaces should be coupled with a protective coating system (Ref 28, p 135). Cathodic protection also generally increases the life of protective coatings by reducing undercutting and lifting due to substrate corrosion. Protective coatings also can be formulated with poisonous compounds to reduce or eliminate biofouling of the submerged surfaces.

Inorganic coatings (such as the zinc-rich paints), hot-dip galvanizing (zinc coating), and aluminizing are also useful methods for protecting steel and other metals when submerged in seawater (Ref 1, p 296).

Cleaning Systems. It is generally accepted that a clean system will be less subject to corrosive attack than a system in which sediment and debris are allowed to accumulate. A well-designed system will tend to remain cleaner for a longer period than a poorly designed system. Eventual accumulation of debris or biofouling is inevitable in a seawater environment, and some critical systems will require periodic or even continuous cleaning in order to maintain the desired operational

characteristics. This is particularly true for heat exchangers and small diameter piping. The effect of this periodic cleaning on the corrosion of the base material or protective coatings must be evaluated. Experience with cleaning of materials that form thin, tightly adherent, corrosion-product films, such as the copper alloys and stainless steels, has shown that these surfaces can be cleaned with little or no adverse effect. Improper mechanical or chemical cleaning can, of course, harm any material. The effect of cleaning on materials that form loosely adherent corrosion-product films, such as steels, can be expected to have considerable adverse effect, as these alloys depend on a buildup of the corrosion products to achieve relatively low corrosion rates (Ref 1, p 44). Removal of these products can result in rapid corrosion.

Protective coatings can also be easily damaged by improper cleaning. This is particularly true at projections and sharp edges. These adverse design features should be avoided on coated systems that require cleaning.

Environmental Design Factors

Intelligent design must consider the environment to which the structure or equipment will be exposed. In some cases, it could be practical to modify the environment to improve the behavior of certain materials.

Seawater is an extremely complex medium that contains nearly all of the known elements. In addition, seawater contains large amounts of complex organic substances, both living and nonliving (Ref 33). Due to the complex nature of seawater and to the local generation, introduction, and consumption of important constituents, the composition of seawater varies considerably with both location and depth in the ocean.

In addition to the chemical factors in the environment, other physical factors must be considered in order to predict and control corrosion of an OTEC plant. Velocity of the seawater is a very important factor and may indeed prove to be a critical factor for such components as heat exchangers. Flow regime, turbulent or laminar, also can affect corrosion and must be considered along with velocity. Other factors, such as temperature, pressure, and heat flow, have been shown to have some effect on corrosion and must be considered in an intelligent system design.

Chemical. Seawater is a complex and nonhomogeneous environment (Ref 34, p 187). Although many chemical constituents of the environment vary considerably with location and depth, experience with ocean structures and corrosion exposure testing has shown that material performance can be correlated with the value of a few key variables. In natural surface seawater, the primary chemical variables of interest are salinity, organic material, and pollution.

OTEC plants will probably be located a reasonable distance from sources of diluent freshwater that would affect salinity to the extent necessary to significantly affect corrosion behavior. Therefore, the

effect of salinity variations in natural surface seawater will be small (Ref 35, p 5). Likewise, the effects of industrial pollution on OTEC systems will be small, unless they are accompanied by a large floating industrial plant. If an OTEC plant will be exposed to either low salinity or polluted waters during construction, maintenance or repair, then careful consideration must be made as to the effect of these variables on material performance. For example, if some copper alloys are initially exposed to polluted seawater, their corrosion resistance upon subsequent exposure to unpolluted seawater will be significantly reduced. Initial exposures to fresh seawater allow these alloys to develop protective corrosion-product films that will improve their corrosion resistance even when subsequently exposed to polluted seawater (Ref 36).

The concentration of organic material in seawater is important in many corrosion processes (Ref 33). The effect of this concentration on the corrosion of metals in surface seawater has not been well studied. Open ocean testing in environments similar to those expected at OTEC operating sites may be necessary to precisely determine the corrosion behavior of materials for critical systems in the OTEC plant.

There is a greater variation in chemicals and corrosion behavior between surface waters and waters at depth than there is between surface waters at various locations. Oxygen content, pH, and organic material concentration and type are the major variables affecting corrosion at depth (Ref 35, p 3-6). The variation of oxygen content and pH with depth in the Pacific Ocean is shown in Figure 8 (Ref 7, p 4). The variations in oxygen content and pH with depth in the Atlantic Ocean are significantly less than those in the Pacific Ocean (Ref 34, p 187). As shown in Figures 9 and 10, the corrosion behavior of some materials varies considerably with differences in oxygen content (Ref 7, pp 15, 213, 214). Recent research has indicated that for some materials, such as aluminum alloy 5052, the variation in pH with depth may have a more significant effect than the variation in oxygen content (Ref 37). Actual environmental exposure tests in the deep ocean have been limited, primarily due to high cost. However, when deep-ocean waters are to be encountered by an OTEC plant, References 1, 7, 10, 16, 17, 34, 35 and 38 through 44 should be consulted in order to obtain valid data for material performance under low velocity conditions.

In addition to the direct effects of variations in environment with depth, these variations can possibly lead to concentration cell attack on electrically conductive members that pass through waters of varying composition (Ref 34, p 188).

Although the accumulation of fouling organisms on exposed surfaces at depth is much less than near the surface, there are organisms present at all depths. The concentration of uncombined organic material may be significantly different at depth. The effect of such differences in organic constituents has not been determined.

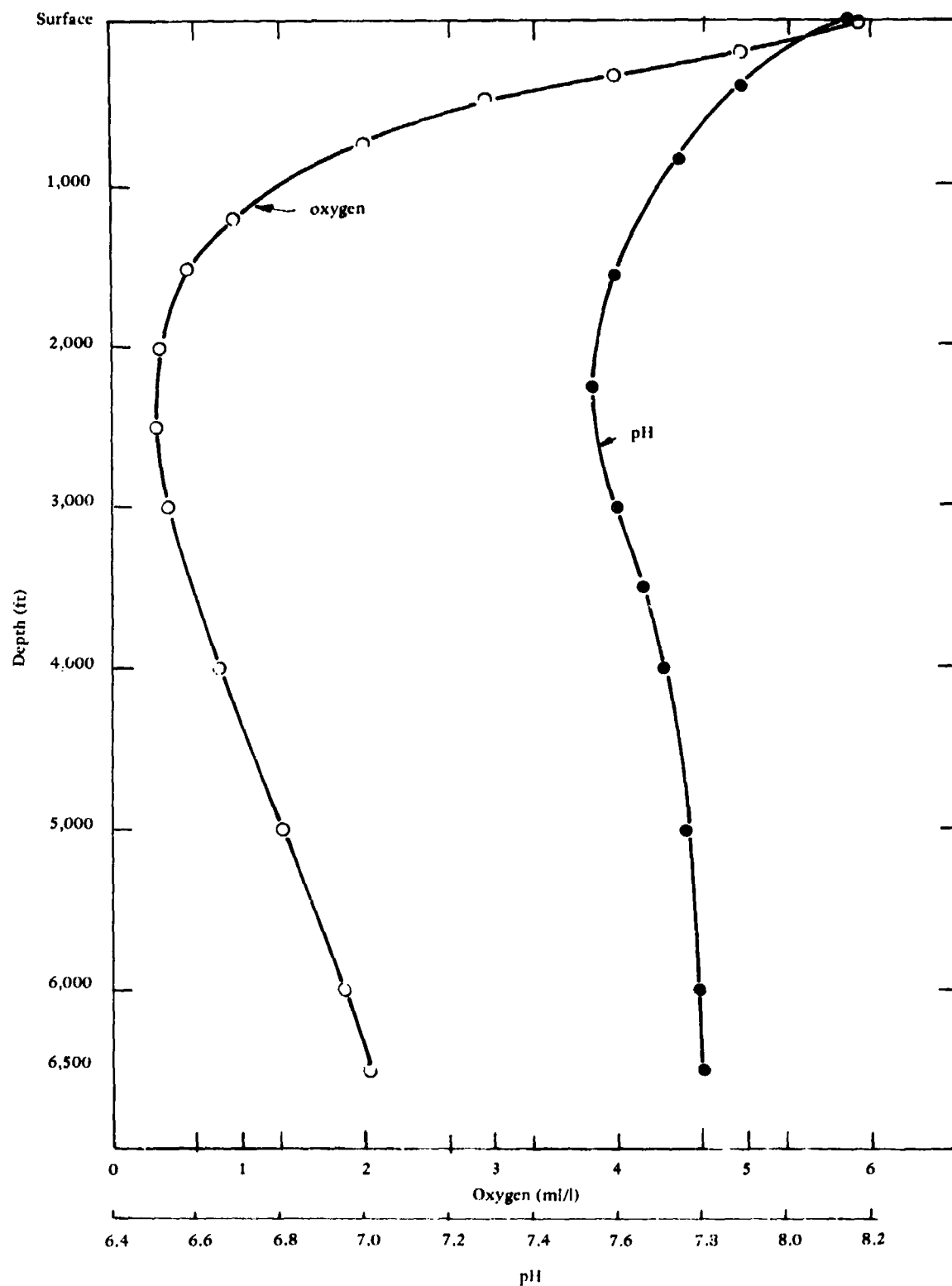


Figure 8. Oxygen content and pH versus depth - Pacific Ocean.

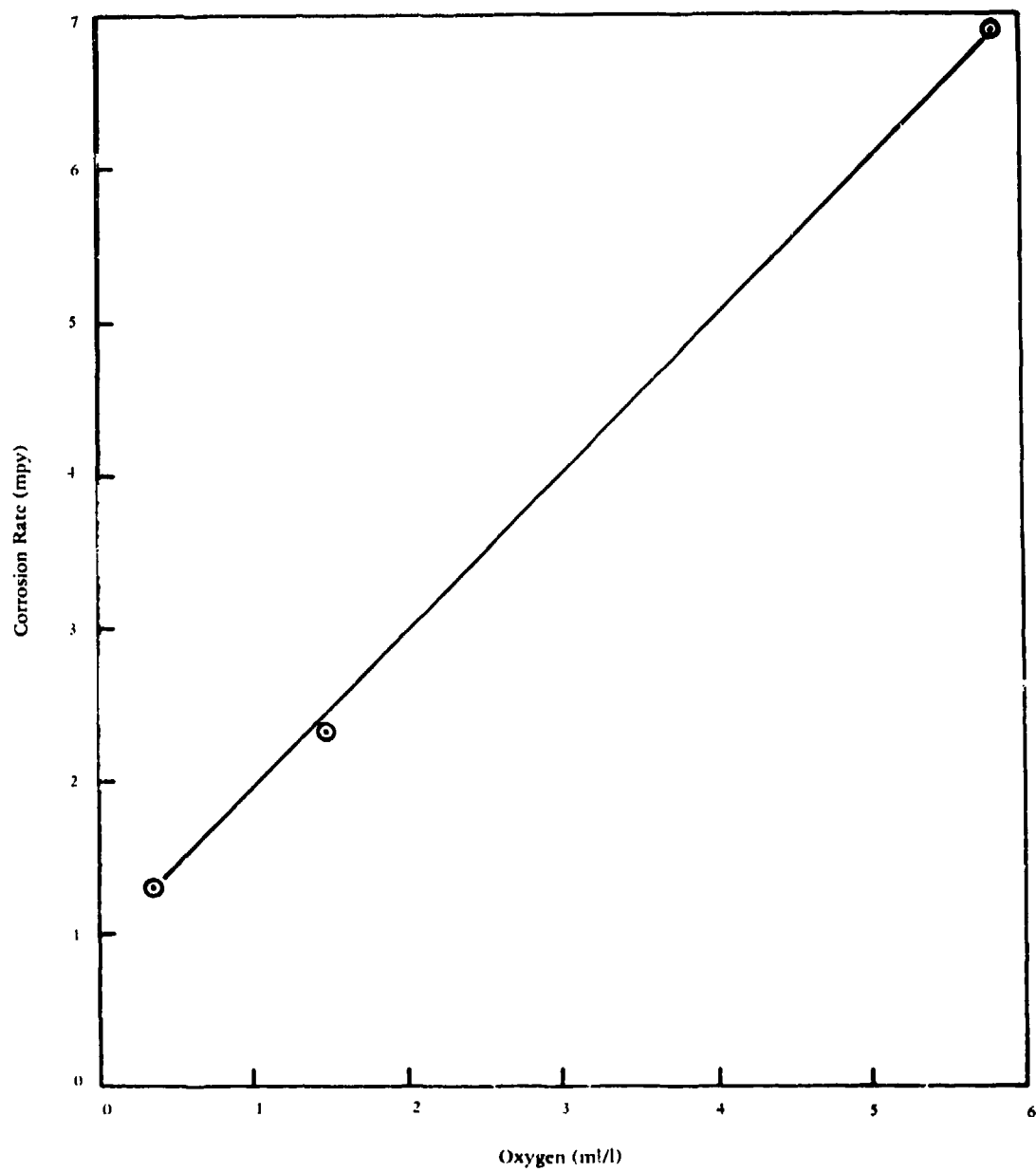


Figure 9. Effect of oxygen content in seawater on the corrosion of steel after 1 year of exposure.

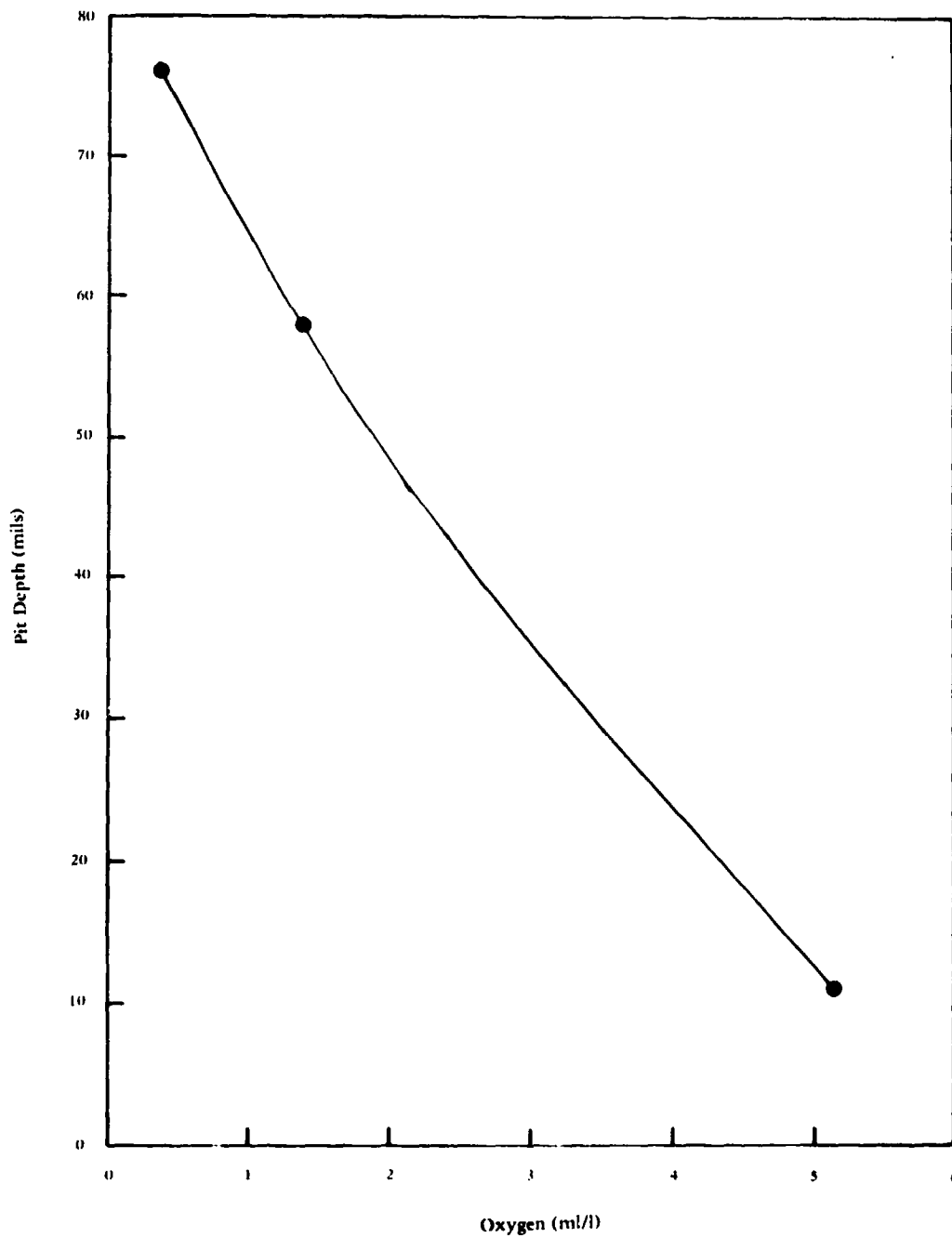


Figure 10. Effect of oxygen content in seawater on the pit depth of aluminum alloy 6061-T6 after 1 year of exposure.

The solubility of several constituents of seawater is also related, either directly or indirectly, to depth (Ref 45). Thus, it is possible that precipitation of materials such as calcium carbonate may occur when deep waters are brought to the surface. Such possible precipitations would have an adverse effect on heat exchanger performance and should be investigated further.

Velocity. Flow velocity may be one of the most significant factors affecting the selection of materials for key components of an OTEC plant. Most materials exhibit satisfactory performance over only a relatively small range of velocity and flow conditions. Aluminum alloys and stainless steels perform well at moderate velocities, but are severely attacked under stagnant conditions. Copper alloys generally exhibit a threshold velocity above which they corrode very rapidly but below which they have satisfactory resistance (Ref 46, p 1745). Materials such as titanium often show no effect of velocity within the limits expected for OTEC plant operation (Ref 1, p 249).

Specific data from corrosion tests, coastal power plants, and ship service may not be directly applicable to the design of an OTEC plant due to the differences in chemical characteristics of the environment and sizes of equipment tested. The reasons for the effect of variations in chemical characteristics are the same as those for low flow conditions as discussed previously. The effect of equipment size on velocity tolerance is more subtle. It has been shown that velocity per se is not the critical factor in the behavior of some alloys. For these, the fluid shear stress at the metal surface is the critical factor (Ref 47). For most equipment, the fluid shear stress is a function of velocity, size, geometry, and fluid viscosity (Ref 48). Thus, the critical fluid shear stress or tolerable shear stress range should be determined for materials that are candidates for critical OTEC systems and should be applied to specific equipment designs. Interim velocity limits can be applied to noncritical candidate materials for validation testing. Such data are presented in References 1, 21, 35, 46, and 49 through 51 as well as in many other documents that outline specific equipment or material performance. From these data the following limiting flow velocities, based on resistance to impingement attack, are suggested for use until more OTEC specific data can be obtained:

| <u>Component</u> | <u>Material</u> | <u>Limiting Maximum Velocity</u> | |
|----------------------|-----------------------------|----------------------------------|---------------|
| | | <u>m/sec</u> | <u>ft/sec</u> |
| Heat exchanger tubes | Aluminum | 1.5 to 1.6 | 5 to 6 |
| | Titanium | no limit | no limit |
| | Stainless steel (A16X) | no limit | no limit |
| | 90:10 copper nickel (CA706) | 3 | 10 |
| Salt water piping | Steel | 1.5 to 1.6* | 5 to 6* |
| | Aluminum | 1.5 to 1.6 | 5 to 6 |
| | Titanium | no limit | no limit |
| | Stainless steel (A16X) | no limit | no limit |
| | 90:10 copper nickel (CA706) | 2.5 to 3.5** | 8 to 12** |

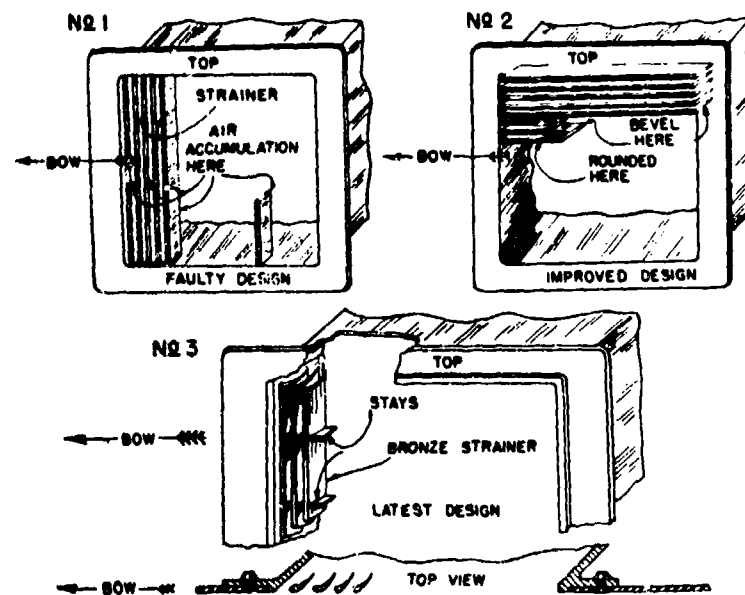
*Based upon corrosion rate of 0.5 mm (0.02 in.) per year. If macro-fouling is present and covers surface, then it is 0.125 mm (0.005 in.) per year.

**Higher limit for larger diameter pipes.

Flow Regime. As discussed in the previous section, the fluid shear stress at the metal surface is the critical variable in the performance of metals under velocity conditions. Under turbulent-versus-laminar flow conditions, the fluid shear stress can vary considerably at a given value of bulk flow due to the variation in Reynolds number or friction factor (Ref 47). Flow regime also affects mass transfer processes which often control corrosion behavior (Ref 52). OTEC heat exchangers will probably operate in the turbulent regime. Both velocity and flow regime must be considered in the determination of fluid shear stresses on metal surfaces. Localized velocity gradients are likely to cause more attack than higher uniform velocities. Damaging velocity gradients are often caused by small radius bends in piping, improperly designed pump discharges, and partially closed (throttled) valves. Debris, such as fouling organisms, that partially obstruct small diameter tubes can also cause damaging velocity gradients and should be avoided by proper upstream screening.

Cavitation-erosion is a drastic form of attack associated with high velocities and high velocity gradients such as are usually encountered in pumps and valves. Critical components, such as impellers, diffusers, and valve trim, should be fabricated from metals such as titanium and high nickel-chromium-molybdenum stainless steels that are resistant to both cavitation-erosion during operation and crevice attack during stand-by periods.

Heat exchanger water boxes are often subject to turbulence-related attack, and the induced turbulence can also affect the performance of the heat exchanger tubes. Proper water box design features are shown in Figure 11 (Ref 21).



Faulty and Improved Design of Injection Strainers for Use on Ships.

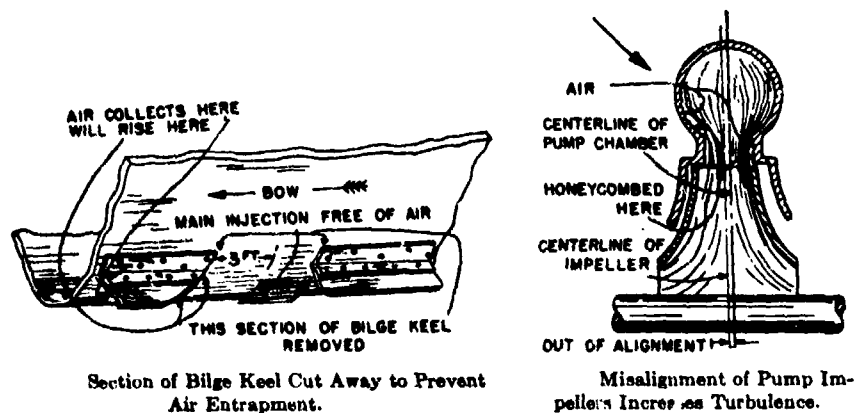
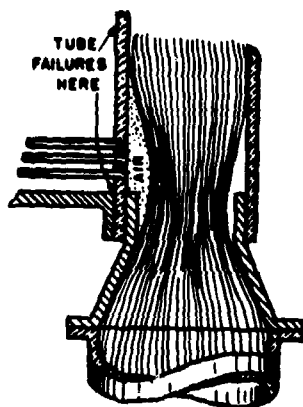
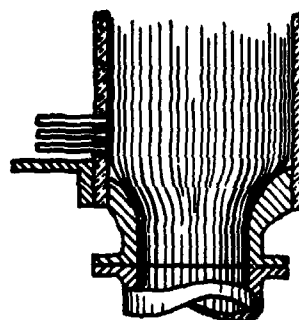


Figure 11. Water box design.

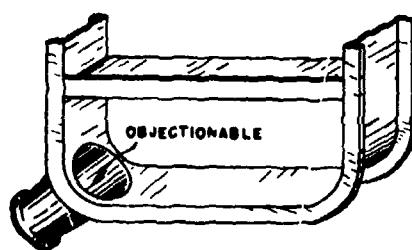


a. *Objectionable.* Restricted entrance due to shallow water box.

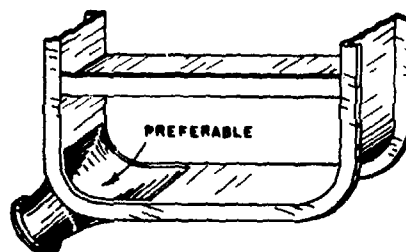


b. *Improved.* Air pocket eliminated by streamlined entrance and deepened water box.

Designs of Injection Nozzle and Water Box.

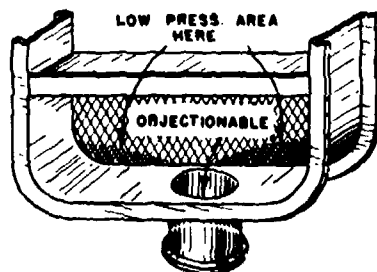


a. *Objectionable.* Sharp angles at junction of nozzle and water box.

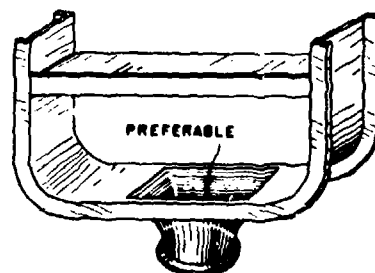


b. *Improved.* Gradually increased nozzle area at approach to water box.

Designs of Entrance to Water Box.



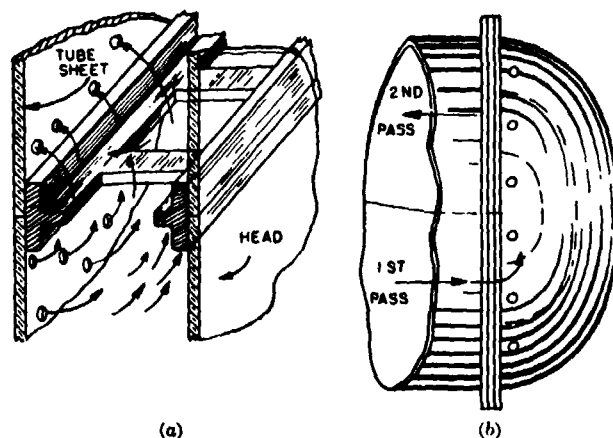
a. *Objectionable.* Cylindrical nozzle; abrupt increase in area.



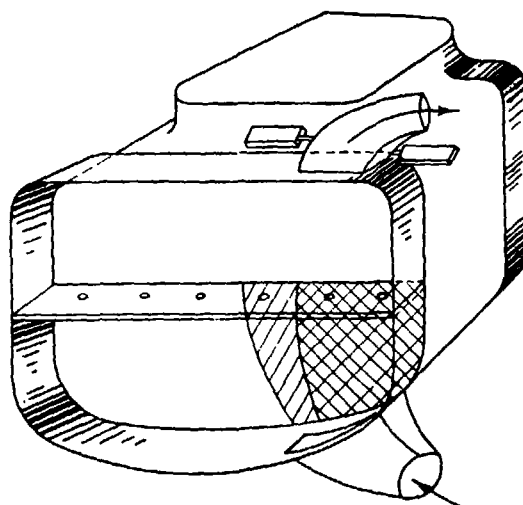
b. *Improved.* Nozzle gradually increasing in area at approach to water box.

Designs of Entrance to Water Box.

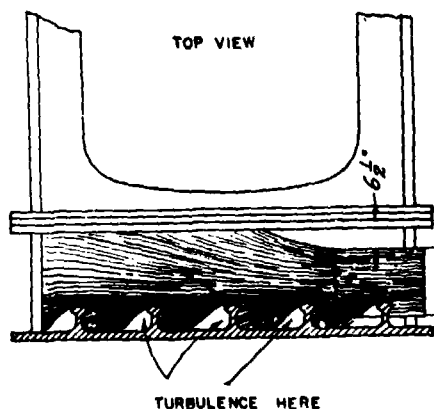
Figure 11. Continued.



(a) Reverse-Flow Water Box with Reinforcing Plate in Center Causes Turbulence and Air Separation in Water Entering Second Pass Tubes. (b) Well-Designed Reverse-Flow Water Box with Test Holes Drilled as Shown.



Injection Nozzle Too Far from Tube Sheet. Air Vents in Division Plate Reduce the Harmful Effect.



Objectionable Internal Reinforcing Ribs in Inlet Water Box.

Figure 11. Continued.

Pressure. Pressure has not been found to have a direct effect on the corrosion behavior of metals (Ref 7,35). Pressure can, aside from mechanical effects such as stress, indirectly influence corrosion behavior. Under high pressure, thermodynamic considerations indicate that a lowering of pH will occur, thus affecting both corrosion and the formation of protective carbonate scales (Ref 35, p 6). Pressure should reduce the tendency of bubbles to form that are responsible for impingement attack (Ref 1, p 124).

Temperature. In surface seawater the effect of temperature on corrosion is generally balanced by two opposing factors. At low temperatures, the solubility of oxygen in the seawater is increased, and the amount of fouling organisms that accumulate on exposed surfaces is low. In high temperature waters, the oxygen solubility is lower, and the fouling accumulations are normally heavier. Thus, the expected increase of corrosion rate with temperature is offset by other factors within the normal range of surface ocean temperatures (Ref 1, p 133).

DESIGN FACTORS INFLUENCING BIOFOULING

There is a natural tendency for any surface exposed to seawater to become covered with biological material. The films formed can range from the thin slimes and sparse macroorganisms typical of the deep ocean to the heavy accumulation of both hard-shelled and soft-bodied plants and animals of the surface. Specific equipment in an OTEC plant will vary greatly in its tolerance to fouling organisms. Considerable amounts of heavy fouling can be accommodated on the platform hull, whereas very thin slime films can adversely affect the performance of heat exchangers. Thus, a wide range of fouling control requirements must be applied to the various OTEC system components.

Fouling organisms also have a direct effect on the corrosion of many materials. Heavy accumulations of growth on steel can limit the access of oxygen to the metal surface and, thereby, reduce corrosion to low values. These low, consistent values are the result of the sulfate-reducing bacteria in sustaining the corrosion of the steel rather than the classical oxygen reduction process (Ref 53). Oxygen and metal ion concentration cells can also be formed by the attachment of certain marine organisms, notably barnacles. These cells can adversely affect the performance of alloys that are susceptible to localized attack, particularly crevice corrosion (Ref 47).

In special cases, mobile organisms, such as sea urchins, can continuously remove protective corrosion product films, thereby producing high corrosion rates (Ref 1, p 14). Sulfides produced by the decay of organisms are a form of natural pollution and should be considered, particularly when alternate filling, stagnation or intermittent anti-fouling treatments are utilized. Organisms, both micro and macro, can also cause accelerated degradation of protective coatings (Ref 1, p 15).

Direct mechanical effects of fouling accumulations must also be considered. The weight and bulk of organisms can increase stresses in equipment, alter flow rates, and cause turbulence, all of which can affect both the short-term mechanical performance and the long-term corrosion behavior of not only the equipment in which the fouling has occurred but also other system components (Ref 1, p 14).

By proper design and fouling control, the accumulation and effects of fouling organisms can be kept within reasonable limits at minimum excess cost. Many factors must be considered in order to obtain optimum (lowest cost for required resistance) fouling control. As in design for corrosion control, these factors can be separated into two broad groups: mechanical and environmental.

Mechanical Design Factors

Mechanical design factors that can influence the attachment and growth of fouling organisms include geometry, orientation, layout, surface finish, cathodic protection, antifouling coatings, and cleaning systems. These factors must not only be considered individually, but must be considered as a synergistic system. Any design is necessarily a compromise. Often factors that decrease fouling will increase corrosion and vice versa. Only by carefully defining required corrosion and fouling resistance and adjusting material selection and design to achieve these requirements can an optimum design be formulated.

Geometry and Orientation. Biofouling will occur on all nontoxic surfaces exposed to ambient seawater. The type and extent of fouling varies considerably with both location and season, and it must either be prevented or tolerated. The major effects of geometry and orientation on fouling are in the area of tolerance rather than prevention. The basic factors of simplicity, accessibility, and maintainability outlined in the corrosion section also apply here.

The adverse effect of biofouling on system performance should be estimated to determine if fouling control is necessary. Fouling mass can be estimated for both near-shore and open ocean conditions (Ref 54). An additional weight of 17 kg/sq m (1.7 lb/sq ft) can be expected on a completely fouled unprotected surface at warm water sites typical of those proposed for OTEC. This is the weight of hard shelled organisms; soft fouling has essentially the same density as seawater. After the surface becomes completely fouled, a stable community is established, and no significant additional weight accumulates. From the surface to a depth of 5 meters (16 ft), surfaces can be expected to be completely fouled within 3 years. At a depth of 18 meters (60 ft), surfaces can be expected to be covered within 12 years. At a depth of 30 meters (100 ft), surfaces will be approximately 50% fouled within 12 years. At a depth of 100 meters (330 ft), surfaces can be expected to be only 5% covered within 12 years. The shape of fouling rate curves indicates that a maximum fouling population will be achieved after 1 to 2 years and will remain fairly stable after that time (Ref 54). The fouling

rate estimations can be used to determine the cleaning interval required. These forecasts are for external surfaces and may not be applicable to the large internal volumes to be encountered in an OTEC plant.

One indirect effect of geometry is that of light on fouling. Fouling organisms are sensitive to light. Light is necessary for photosynthesis, and plants will not grow in its absence. Animal species, however, seem to flourish in dark areas. Thus, the maximum amount of fouling seems to occur on strongly illuminated or completely dark surfaces (Ref 55). This effect should be considered as a predictive tool, not a preventive measure (Ref 56).

The increase in resistance to fluid flow due to fouling is also an adverse effect. Data from fouling of ships' hulls and increase fluid flow resistance in small diameter piping can be used only to estimate these effects on the interior portions of an OTEC plant.

The effect of fouling on heat transfer surfaces is a critical factor in the viability of the OTEC concept (Ref 57). The geometry of the heat transfer surfaces will have little direct effect on their propensity to foul, but it will have a significant effect on the efficacy of various antifouling treatments. Geometry can, however, indirectly affect the fouling of heat transfer surfaces by influencing other factors, such as velocity and turbulence, which will be discussed later in this paper.

Orientation of a surface has a direct effect on the fouling of that surface. In general, the lower side of a horizontal surface fouls more heavily than the upper side of a horizontal surface, with there being a gradation of intensity between these extremes (Ref 55). The variation is small, however, and, taking the vertical orientation as an average, will vary approximately $\pm 10\%$ (Ref 54).

Layout. Like geometry and orientation, layout does not have a significant direct effect on fouling. The indirect effects of layout on accessibility, maintainability, etc., which were outlined in the preceding section on corrosion, apply also to fouling.

Surface Finish. There have been some studies made that indicate a polished surface is initially more resistant to fouling than a roughened one (Ref 58). This effect seems to be short-lived, and the fouling on polished surfaces approaches that on roughened surfaces within a few months (Ref 58). Considerable information on other surface characteristics was located, but it was primarily related to surface chemistry and material properties.

Metals can be grouped into three broad categories of fouling properties. Highly corrodable metals, such as steel, foul readily. The fouling can, however, be readily removed with the typical loose corrosion products formed. Passive metals, such as the stainless steels, will also readily foul, but the fouling is tightly adherent. Some metals, such as the copper alloys, form corrosion-product films (in this case, cuprous oxide) that are toxic to organisms (Ref 59).

The fouling resistance of inorganic materials is related primarily to the initial adhesion of a proteinaceous "conditioning film," which serves as a substrate for the attachment of subsequent fouling communities (Ref 60). Surface tension appears to have primary influence on the adhesion of these films. Surface tension in the range of 20 to 30 dynes/cm appears to result in a minimum adhesion, although a totally fouling free surface has not been achieved through application of this phenomenon (Ref 60).

Cathodic Protection. Cathodic protection, or rather the imposition of electrical currents, has been widely studied as an antifouling measure (Ref 61-63). Except for the in-situ generation of chlorine gas (Ref 62) these methods are considered either ineffective or impractical for large surfaces, primarily due to the high current densities required for protection (Ref 64,55). The dissolution of heavy metals from coatings or alloy matrices by anodic currents and the periodic formation and removal of calcareous coatings by periodically reversed currents may, however, be applicable to certain critical systems where no other means of fouling control is practical. Some studies indicate that steel protected with low current densities (1 to 30 mA/sq m) may be subject to heavier fouling than unprotected surfaces. With currents above 30 mA/sq m, fouling was reduced (Ref 55).

Antifouling Coatings. Antifouling coatings that contain toxic materials can be used to prevent fouling. However, these coatings have limited life, because the toxic materials must leach from the coatings in order to provide fouling resistance. Unless the system can be dewatered and recoated, antifouling coatings should be considered as a temporary measure. If the equipment was properly designed to allow for such dewatering and recoating, then such coatings could be practical in some instances. The selection of these coatings for specific applications is outside the scope of this report. Certain precautions must be taken, however, in the selection of antifouling coatings in order to prevent adverse corrosion effects. The toxic products from antifouling coatings containing heavy metals, such as copper and mercury, can cause rapid corrosion of some metals, particularly aluminum alloys. These coatings should not be applied directly to aluminum surfaces, nor should seawater flowing past them be allowed to contact aluminum surfaces (Ref 1, p 18).

Radioactive coatings can prevent fouling, but, for the coatings developed to date, the levels of activity required present serious safety and environmental problems (Ref 63).

Cleaning Systems. Fouling can be removed from any surface by mechanical cleaning. Initial proteinaceous and bacterial films can be removed by simply wiping or brushing, whereas hard-shelled organisms require vigorous scraping to dislodge them from many surfaces. The design of a system will be a major factor in the efficacy of any cleaning system. Smooth and simple surface contours lend themselves to easy cleaning, whereas complex contours with re-entrant angles, etc., are

more difficult to clean. For example, the interior of heat exchanger tubes are relatively simple to clean whereas their exterior surfaces, particularly when they are closely spaced, present a much more difficult situation.

Environmental Design Factors

By properly controlling or modifying the chemical or physical character of seawater, the ability of fouling organisms to live and grow can be limited or totally inhibited. Any modification of the large volumes of seawater required for the operation of an OTEC plant will require large inputs of chemicals or energy. Therefore, the use of environmental modification as an antifouling method should be carefully analyzed. Certain environmental factors will be modified by the normal operation of the plant and, where possible, the effect of these modifications on fouling should be used to the maximum overall benefit.

Chemical. Introduction of toxic materials into the environment can kill marine organisms. Chlorine is the most widely used chemical agent for this purpose. Chlorine may be added as a gas or as a hypochlorite (Ref 65). It can also be generated in situ by electrolysis of the seawater itself (Ref 66). Chlorine residuals on the order of 0.25 ppm applied continuously will provide complete control in most instances. Chlorine additions must, of course, be in excess of these residual requirements in order to allow for reaction of the chlorine with the seawater (Ref 65). The amount of chlorine required will vary considerably with local conditions (Ref 65). This may be particularly true for deep-ocean waters where the fouling population is limited. The intermittent addition of chlorine can also eliminate fouling (Ref 67, p 359). The actual amount and optimum addition cycle of chlorine for inhibiting fouling in the various portions of an OTEC system can be expected to be significantly different from the dosages normally used in coastal plants. Specific recommendations as to the feasibility of chlorination as the method for inhibiting fouling of an OTEC plant cannot be made until these data are obtained.

Velocity. Relative velocity between seawater and a surface can inhibit or prevent the attachment of fouling organisms (Ref 1, p 132). The velocity of this flow is the major antifouling factor that can be directly controlled by system design. While the critical velocity required to inhibit or prevent fouling has not been well defined, it probably lies in the 2-to-4-fps range (Ref 63). The use of velocity to control fouling depends on continuous flow. If the flow is interrupted, even for short periods, fouling organisms will attach and continue to grow under subsequent high velocity conditions (Ref 65, p 39). Thus, in order to be practically applicable to OTEC systems, the use of velocity to control fouling probably will need to be combined with some other antifouling method in order to accommodate periods of low flow.

Design also affects the uniformity of velocity and, thus, the efficacy of velocity in inhibiting fouling. Where the flow is not smooth and evenly distributed, areas of low velocity will occur and, if

below the critical velocity, fouling will occur. Fouling downstream of obstructions, such as elbows, screens, etc., is common even in systems operating at high velocity. It is suggested that an approach analogous to the surface fluid shear concept for velocity effects on corrosion (Ref 47) may be applicable to the study of the effects of velocity on fouling.

Temperature. Temperature has a significant effect on fouling organisms and, thus, on fouling rates. In warm, tropical waters the fouling rates are typically high, whereas they are typically lower in temperate waters. A rapid temperature change on the order of 20 to 40°C can inhibit or prevent fouling (Ref 63,68,69). However, providing for such temperature changes in the volumes of water involved in the operation of an OTEC plant presents many engineering and economic difficulties. It is possible that the effect of heating may be significantly greater on deep ocean organisms than on common surface organisms (Ref 70, p 28).

Pressure. The effect of pressure, or rather changes of pressure, on fouling organisms is not well documented. As OTEC will bring large quantities of deep water to the surface and utilize this water in equipment, such as heat exchangers, that have critical fouling requirements, this effect must be studied further. It is generally assumed that fouling will be minimal in the deep water, even when brought to the surface. The heavy accumulations of typical hard fouling found in heavy surface exposures do not generally occur in deep waters, but the marine organisms capable of forming slime films and heavier accumulations of animal fouling are known to occur at all depths proposed for OTEC plant operations (Ref 71). The effect of these organisms on OTEC plant condensers should not be neglected, unless valid test data can be obtained that show the fouling rates are within acceptable limits.

SUMMARY

Many factors that influence the biofouling and corrosion of OTEC system surfaces can be manipulated by system design. In general, simple designs are preferable to complex designs; maintainability and accessibility are key factors; and, as for any engineering endeavor, the final design will be a compromise between many factors. In some instances, corrosion and biofouling will be of little concern, while the influence of other factors will predominate. In other instances, corrosion and biofouling will be critical factors and will predominate over other concerns. Careful attention to details of design and application of the basic design principles outlined in this report is necessary to control biofouling and corrosion of an OTEC plant. Only by a careful balance of these many factors through careful engineering judgment can an optimum OTEC plant be placed into successful operation.

RECOMMENDATIONS

Because of the unique nature and scale of the OTEC concept, much extrapolation of presently available experience and experimental data must be made to obtain a first approximation of the biofouling and corrosion behavior that may occur in a full-scale OTEC plant. Such topics as the rate of biofouling of heat exchanger tubes in the open ocean using both near-surface and deep-ocean water, the precipitation of materials from deep water when brought to the surface, the effect of environmental gradients on structural attack, the effect of velocity on the corrosion of very large components, as well as many other OTEC specific problems must be studied under actual OTEC conditions in order to refine the ability to predict and control biofouling and corrosion in an OTEC plant.

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Appendix

FORMS OF CORROSION ATTACK

For all the combinations of metals, ocean environments, and structural applications, only a few forms of corrosive attack occur. Several corrosion mechanisms may result in the same form of attack in various situations. The description of these forms of attack given below are intended to provide the design engineer with a mental picture so that the effect of the attack on structural integrity or equipment operation can be better evaluated.

1. No Corrosion. While, strictly speaking, this is not a form of attack, it is a form of material behavior exhibited by a few alloys. In this form of attack there is essentially no interaction with the marine environment and no change in weight, strength, ductility or other property that can be attributed to the marine exposure. Typical materials that undergo no corrosion when exposed to seawater are: platinum, gold, titanium (selected alloys), nickel alloys (N06625* and N10002*), cobalt alloy (R30035*), and the complex stainless steel Al6X.

2. Uniform Corrosion. When a metal corrodes at substantially the same rate over its entire exposed surface, uniform corrosion is said to have occurred. As for all natural phenomena, the attack is not strictly uniform. Surface roughening always occurs. The amount and distribution of this roughening vary considerably and can grade into pitting corrosion. Weight loss is a valid measurement of uniform corrosion. Typical materials that are subject to uniform corrosion in seawater are carbon steels and most alloy steels (when mill scale has been removed), copper, beryllium copper (C17200), and 90-10 copper-nickel (C70600).

3. Pitting Corrosion. Pitting is a form of localized attack where the corrosion rate is substantially greater on some areas of a metal surface than on others. The result of pitting attack can range from broad, shallow cratering to narrow, deep pits resembling drilled holes. The surfaces surrounding the pits can remain virtually unattacked. Weight loss cannot be used to evaluate pitting corrosion. Pit depth and frequency measurements, tensile tests, and visual observations are normally used to evaluate pitting attack. The gradation of uniform corrosion into the broad, shallow cratering form of pitting attack can be subtle. The two forms of attack can be differentiated by use of the pitting factor (P.F.) where

$$P.F. = \frac{\text{Depth of Deepest Pit}}{\text{Average Depth of Attack}}$$

*Numbers refer to assignments in "Unified Numbering System for Metals and Alloys," Society of Automotive Engineers, SAEJ 1086, latest issue.

When the pitting factor is less than two, uniform corrosion is said to have occurred. When the pitting factor is greater than two then pitting corrosion is said to have occurred. Typical materials that are subject to pitting attack are the aluminum alloys and stainless steels, except those containing appropriate amounts of nickel and molybdenum such as the Al6X stainless steel proposed for OTEC applications.

4. Galvanic Corrosion. Galvanic corrosion is attack accelerated by electrical coupling of two or more dissimilar metals. Galvanic attack can occur rapidly and can result in either uniform or localized attack. Not only the composition of the metals involved, but also their relative exposed surface areas, distance apart, geometric distribution, and the resistance of the electrical contact, determine the rate and type of attack that will occur. Galvanic corrosion tendencies in seawater can be predicted. In most cases, however, quantitative galvanic corrosion rates cannot be predicted. Galvanic corrosion should, therefore, be avoided wherever possible by electrically isolating dissimilar metals. Although nearly any metal can be subject to galvanic corrosion, the aluminum alloys, carbon, and alloy steels are most prone to this type of attack due to their relatively high activity in seawater.

5. Concentration Cell (Crevice) Corrosion. Concentration cell corrosion is attack caused by a difference in environment between different points on a single metal. While differences in temperature, light, etc., can cause concentration cell corrosion in special circumstances, the most common cause of concentration cell corrosion in marine environments is the differential environment caused by the trapping of seawater in small gaps or crevices. When the seawater is trapped and held in a crevice, its composition will change considerably from that of the bulk seawater outside the crevice. For some materials, such as the aluminum alloys and stainless steels, the composition change of significance is the consumption of dissolved oxygen within the crevice. This, combined with changes in acidity within the crevice, results in accelerated attack within the crevice. This form of attack is insidious, because it can occur rapidly and is often revealed only by equipment failure.

A second form of crevice attack is commonly found to occur on the copper alloys. In this form of attack, the buildup of metal ions within the crevice causes the area inside the crevice to become less active than the area just outside the crevice. Accelerated attack occurs just outside the crevice. Weight loss cannot be used to evaluate this form of localized attack. Depth and frequency of attack are often used to evaluate crevice corrosion.

6. Dealloying. Dealloying is the selective attack of one constituent of an alloy. As alloys, by definition, consist of solutions or mixtures of more than one element, it is possible that, in some instances, one or more constituent of the alloy will be sufficiently more active than the bulk alloy to be subject to selective attack. In most cases the residual material is porous and spongy and has little mechanical strength. Typical materials subject to this form of attack in

seawater are the cast irons, yellow brass (C27000), and aluminum bronze (C95400). Weight loss cannot be used to properly evaluate this form of attack. Penetration of the attack into the metal as measured on a cross section is often the method of evaluation.

7. Intergranular Corrosion. Intergranular corrosion is the internal attack of a metal at or adjacent to the grain boundaries. All engineering materials are agglomerations of individual crystals or grains. The areas where these grains meet are called grain boundaries. In some metals, such as some aluminum alloys, the grain boundaries themselves are more active than the bulk material. In other alloys, such as the stainless steels, improper heat treatment (sensitization) can lead to rapid attack of the material adjacent to the grain boundaries. In both cases, the structural integrity of the alloy is essentially destroyed in the affected area with a very small amount of actual material loss. Weight loss cannot be used to evaluate this form of attack. Microscopic examination and tensile testing are the most commonly used methods of evaluation.

8. Stress Corrosion Cracking. Stress corrosion cracking results in the failure of a component in a shorter time at a given load or a lower load in a given time when exposed to static stress in a particular environment as compared to failure loads or times in air. Stress corrosion cracking can occur rapidly and often occurs due to residual fabrication stresses rather than service loading. High strength materials are most susceptible to this form of attack. Typical materials subject to this form of attack in seawater are some aluminum alloys, some titanium alloys, and some precipitation-hardening stainless steels. Failures of structures by stress corrosion cracking can be predicted by fracture mechanics techniques when, by experiment, critical stress intensity factors for the specific materials have been determined.

9. Corrosion Fatigue. Corrosion fatigue is the dynamic analogy of stress corrosion cracking. In this form of attack failure occurs at a lower stress level or in a fewer number of cycles when exposed to cyclic loading in an aggressive environment than when exposed to cyclic loading in air. Although nearly every material will show some effects of corrosion fatigue, the most significant reductions are noted on materials such as mild steel, ultra high strength steels, and some copper alloys. Reductions to as little as 5 to 10% of the in-air fatigue strength are not uncommon.

10. Hydrogen Embrittlement. Hydrogen embrittlement is similar to stress corrosion cracking in its effect on the load-bearing capacity of a material. In some cases, these two forms of attack are identical. The source of hydrogen can be from initial manufacture, electroplating, cathodic protection, the presence of sulfate-reducing bacteria, or self corrosion of the material itself. Ultra high strength steels are most susceptible to this form of attack as are many other materials, such as some stainless steels.

11. Erosion Corrosion. Erosion corrosion is the attack of a metal caused by the rapid flow of a fluid past or the impingement of a fluid on the metal surface. Steels, copper alloys, and aluminum alloys are most subject to this form of attack in seawater.

12. Cavitation Corrosion. Cavitation corrosion is the result of the impingement and collapse of vacuum bubbles on a metal surface. The bubbles are normally formed in areas of low pressure in a high velocity stream, such as are commonly found downstream of obstructions to the fluid flow. Cavitation corrosion is particularly severe on copper alloys, steels, and aluminum alloys and should be avoided by proper hydraulic design.

13. Fretting Corrosion. Fretting corrosion is attack accelerated by relative motion between two surfaces in close contact. The attack may be due to the repeated rupture of inherently protective corrosion product films or may be due to direct abrasion effects with the corrosion products serving as an abrasive. Fretting corrosion can result in rapid attack and should be avoided by design such that relative motion between faying surfaces is avoided. Fretting corrosion of aluminum heat exchanger tubes at tube supports is an example of this type of attack. Welding of joints is an effective method of preventing fretting corrosion.

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